

Adsorption behavior of Zr(IV) and Hf(IV) on a silica-based macroporous TODGA adsorbent

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Abstract In order to separate Zr(IV) and Hf(IV) in acidic solution, several kinds of silica-based macroporous adsorbents were synthesized. Their adsorption selectivity for Zr(IV) and Hf(IV) in HCl solution was investigated, and the TODGA adsorbent for the two elements had the largest adsorption difference. The effects of acid type, HCl concentration, and temperature on the adsorption behavior of Zr(IV) and Hf(IV) onto the TODGA adsorbent were conducted by batch experiments. It was found that H^+ exhibited a quite strong influence on adsorption capacity of Zr(IV) and Hf(IV). Isotherm fitting showed that the Langmuir model agrees well with the experimental data. The thermodynamic parameters indicate that the adsorption processes for both elements are endothermic reactions. The TODGA adsorbent had the higher adsorption selectivity for Zr(IV) over Hf(IV) and could be promising for their mutual separation.

Key words Zirconium, Hafnium, TODGA/SiO₂-P, Adsorption characteristics, Selective separation

1 Introduction

Zirconium and hafnium, a pair of co-existing elements, are commonly used as engineering materials in nuclear industry for their specific nuclear properties. Zircaloy is generally used as structural components in reactor cores for its low thermal neutron capture cross-section, whereas hafnium alloy has been employed as controlling materials because of its 640 times higher neutron adsorption cross-section. The hafnium ratio in zirconium has a direct effect on the safety and efficiency of the reactor cores. Therefore, the nuclear grade zirconium sponge requires to contain hafnium of less than 100 ppm^[1,2]. However, as brother symbiosis of the same subgroup, their chemical similarity is greater than that of any other two elements in the periodic table (atomic radius: Zr=0.145 nm, Hf=0.144 nm; ionic radius: Zr(IV)=0.074 nm, Hf(IV)=0.075 nm)^[3]. The mutual separation of Zr and Hf is recently of intriguing interest in the area of nuclear industry.

Numerous processes for separating zirconium and hafnium have been conducted, and there are only

three established technologies in industrial scale, i.e., the multiple crystallization of potassium zirconium fluoride, the solvent extraction using methyl isobutyl ketone (MIBK) or tributyl phosphate (TBP) or tri-n-octylamine (TOA) and the extractive distillation of the chlorides^[4-6]. There are still many problems inherent inextricable in these processes, such as emulsification, flooding and loading limits, sophisticated technologies, phase disengagement, and large solvent consumption^[7]. Recently, increasing environmental concern and energy consumption lead to the search for a new effective separation process.

One of the most efficient methods is the adsorption and separation based on solid phase, for example, the organic (synthetic/natural) or inorganic adsorbents can be treated as extraction chromatography^[8]. In extraction chromatography, an inert support either alone or in combination with a suitable diluent is impregnated with an organic extractant, producing a solid sorbent capable of selectively removing certain metal ions. In brief, the extraction chromatography combines the selectivity of the solvent extraction process with the simplicity and

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multistage character of the column chromatographic system, so it has some attractive advantages such as minimal organic solvent utilization, less waste accumulation, compact equipment, simple operation and simultaneous separation of multi-components. Hence, as an alternative separation method, the extraction chromatography used for separation of zirconium and hafnium is desirable^[9,10].

An ideal extractant in separation process should consist only of C, H, O, and N atoms rather than S or P atoms to make them combustible to gaseous products after utilization. In recent years, a chelating agent, *N, N, N', N'*-tetraoctyl-3-oxapentane-1, 5-diamide (TODGA) containing no S or P atoms is attracting extensive attentions as a promising extractant to separate high-valence metal ions. There have been many reports on its systematic adsorption ability to various elements^[11–16]. A. Sh. Saleh *et al.* investigated the extraction behaviors of zirconium and hafnium by TODGA, indicating the effective extraction from $\text{HNO}_3 \geq 3 \text{ mol/L}$ ^[17]. Also, several other extractants abbreviated as BTP, Calix[4] arene-R14 and HDEHP were extensively used to separate Zr and Hf^[18–20]. The present work mainly deals with preparing a silica-based macroporous TODGA adsorbent, exploring the optimum adsorption condition and mechanism of Zr(IV) and Hf(IV) from HCl solution.

2 Experimental

2.1 Materials

A neutral chelating agent, TODGA (more than 96.5 % purity), the BTP, Calix-arene-R14, and HDEHP (Kanto Chemical Co. Inc.) were used without further purification. The silica-based polymer support ($\text{SiO}_2\text{-P}$) was synthesized as described previously^[21]. The symbol (P) contained in the $\text{SiO}_2\text{-P}$ particles refers to the styrene–divinylbenzene (SDB) copolymer prepared by means of a polymerization reaction inside the macroporous SiO_2 substrate. The Zr(IV) and Hf(IV) standard solutions (1000 mg L^{-1}) were from Alfa Aesar. Zirconium oxychloride ($\text{ZrOCl}_2\cdot\text{H}_2\text{O}$, 99.8%) and hafnium tetrachloride (HfCl_4 , 99.9%) were from J & K Scientific Ltd. Dichloromethane, dodecyl-benzenesulfonic acid, methanol, HCl, and NaOH

standard solutions and other chemicals were all analytical reagent (Sinopharm Chemical Reagent Co. Ltd.). The distilled water was further purified using a Milli-Q (Millipore) system ($18\text{-M}\Omega$ resistance) and used throughout the experiments.

2.2 Preparation of adsorbents

In order to improve affinity between $\text{SiO}_2\text{-P}$ particles and extractant, the $\text{SiO}_2\text{-P}$ particles were activated by methanol as follows. The $\text{SiO}_2\text{-P}$ particles were mechanically mixed with the methanol in a conical flask for about 1 h at the 20 r/min, and separated using a sintering glass filter of $0.45 \mu\text{m}$ pore. The similar operation was repeated three times. The activated $\text{SiO}_2\text{-P}$ particles were dried in a vacuum oven at around 313 K for 12 h. The TODGA/ $\text{SiO}_2\text{-P}$ was synthesized as follows.

The immobilization and impregnation of TODGA into the $\text{SiO}_2\text{-P}$ particles and the polymerization reactions inside $\text{SiO}_2\text{-P}$ particles were performed under the vacuum state. The weighted quantity of extractant was dissolved completely in dichloromethane (200 mL) and the double amount of the activated $\text{SiO}_2\text{-P}$ particles were weighed accurately, mixed into a conical flask (300 mL), and stirred mechanically for 120 min at room temperature. For Calix[4]arene-R14 adsorbent, it also needed to simultaneously add proportional dodecyl benzene sulphonic acid as a molecule modifier. Then the mixture was moved subsequently into a silicon-oil bath and further stirred at about 313 K for 120 min to impregnate and immobilize TODGA molecule into the pores of the $\text{SiO}_2\text{-P}$ particles. The operation temperature in synthesis process was kept using an EYELA OHB-2000 Model temperature controller (Tokyo Rikakikai Co. Ltd., Japan). The impregnation process was continued until almost all of organic solvent, i.e. dichloromethane, was evaporated. Following drying in a vacuum drying oven at around 313 K overnight, light yellow macroporous silica-based polymeric composite was obtained.

Thermal stability of the adsorbent was evaluated by a thermal gravimetry analyzer (Shimadzu T-60) at the operating temperature range from 30–600 °C with a heating rate of $2 \text{ }^\circ\text{C min}^{-1}$ under oxygen atmosphere.

2.3 Batch adsorption experiments

The adsorption evaluation of the adsorbent was conducted using a thermostatic water bath shaker in a wide range of acidity, metallic ions concentration and temperature. All solutions used for adsorption were freshly prepared because both Zr(IV) and Hf(IV) metal ions are apt to hydrolyze and polymerize. The concentration of mineral acids in aqueous phase was investigated in the range of 0.1–8.0 mol/L and the operation temperature was controlled in the range of 298 K–323 K. The phase ratio was 0.05 g of adsorbent to 5 cm³ of solution. A weighed quantity of adsorbents was put into a 10 cm³ glass flask with 5 cm³ solution described above, then the mixture was shaken at 120 r/min for determined contact time under given temperature. After phase separation through a membrane filter with a mean pore of 0.45 μm, the concentrations of Zr(IV) and Hf(IV) metal ions before and after adsorption in aqueous phase were determined utilizing an ICP-AES instrument (Shimadzu ICP-7510). The equilibrium adsorption capacity (Q_e , mmol/g), distribution coefficient (K_d , cm³/g) and separation factor (SF) were calculated as follows.

$$Q_e = [(C_0 - C_e)/M](V/m) \quad (1)$$

$$K_d = [(C_0 - C_e)/C_e](V/m) \quad (2)$$

$$SF = K_{d,Zr} / K_{d,Hf} \quad (3)$$

where C_0 and C_e denote the initial and equilibrium concentrations in aqueous phase (mg/L); M means the molar mass of Zr and Hf; m represents the mass of adsorbent, g; V (cm³) is the volume of the aqueous phase used in the experiment.

3 Results and discussion

3.1 Screening of adsorbents

In order to choose the optimum adsorbent to separate Zr(IV) and Hf(IV), adsorption selectivity with different adsorbents was firstly investigated in batch experiment under the same metal ions concentration in HCl solution. Fig.1 shows the variational distribution coefficient and separation factor of Zr(IV) and Hf(IV) with different adsorbents. The results indicated that the TODGA adsorbent had the largest SF between Zr(IV) and Hf(IV), though the HDEHP adsorbent had the maximal adsorption capacity. As a result, the TODGA adsorbent was chosen as the candidate adsorbent in the

next experiments for its excellent separation and friendly environment.

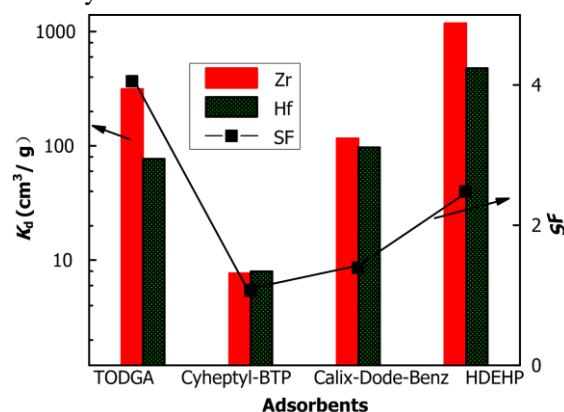


Fig.1 K_d and SF of Zr(IV) and Hf(IV) in HCl solution with different adsorbents V/m : 100 cm³/g; [Metal]: 2.5 mmol/L; [HCl]: 1 mol/L; 303 K; Speed: 120 r/min; Contact time: 12 h.

3.2 Characterization of adsorbents

The microscopic image were shown in Fig.(2).

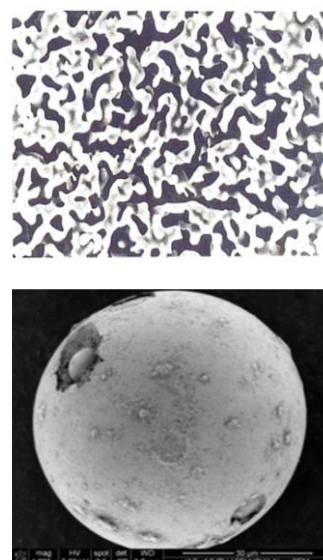


Fig.2 SEM images of porous SiO₂-P support and TODGA / SiO₂-P adsorbent (upper: SiO₂ inner, lower: TODGA/ SiO₂-P).

The TG-DTA curves for TODGA/SiO₂-P indicated that there were obvious weight losses at about 300 °C due to thermal decomposition of styrene-divinyl benzene (SDB) copolymer which could be abbreviated as the letter 'P' in the SiO₂-P. The overall weight loss of SiO₂-P was estimated to be 16.9%, it meant that 16.9 wt% SDB had been polymerized inside the SiO₂ substrate. As for TODGA/SiO₂-P, the TG curve appeared two weight loss peaks at around 200 °C and 300 °C. This indicates that the TODGA mainly decomposed at about 200 °C. The TG-DTA,

composition of TODGA/SiO₂-P adsorbent was determined as: TODGA, SDB and SiO₂ share 33.1, 11.3 and 55.6 wt%, respectively. Generally, the adsorption capacity of adsorbents increases with the content of TODGA impregnated inside SiO₂-P particles. However, it was observed that when the

content of TODGA was higher than 33.3%, the redundant TODGA molecules could not enter the pores of the SiO₂-P particles and only adhered on the particles surface^[22], as shown in Fig.3. The physical and chemical parameters of the SiO₂-P and TODGA/SiO₂-P are listed in Table 1.

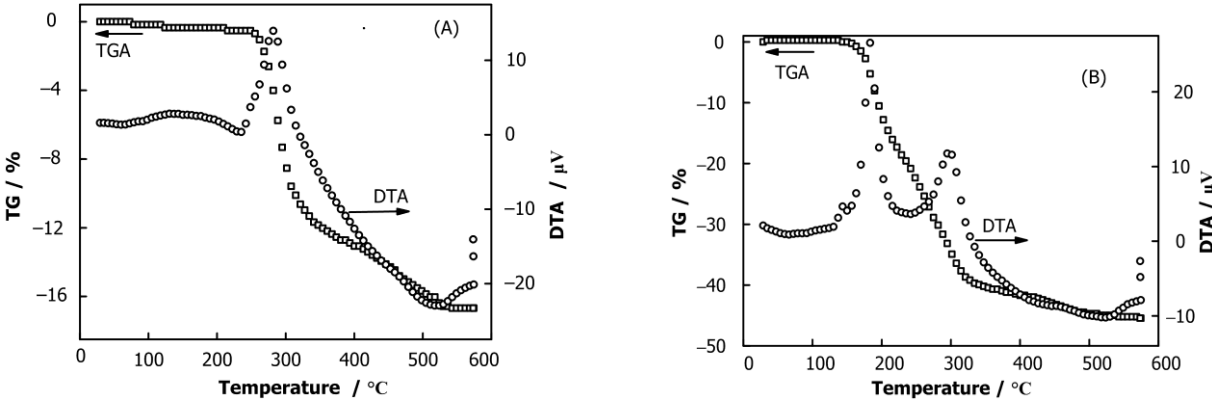


Fig.3 TG/DTA curves of SiO₂-P (A) and TODGA/SiO₂-P (B) under Oxygen atmosphere.

Table 1 The physical and chemical parameters of TODGA/SiO₂-P adsorbent

Physical parameters of SiO ₂ -P		Chemical component of TODGA/SiO ₂ -P			
Mean pore size	50 nm	Unit of analysis	SiO ₂ (wt%)	SDB(wt%)	Solvent (wt%)
Bead diameter	40–60 μm	SiO ₂ -P in synthesis	81.6	18.4	/
Spe Surface area	80 m ² /g	SiO ₂ -P in TGA	83.1	16.9	/
Pore volume	1.0 cm ³ /g	in synthesis	54.4	12.3	33.3
SDB inside	/	Adsorbents in TGA	55.6	11.3	33.1
SiO ₂ -P support	/	/	/	/	/

3.3 Effects of variety and concentration of acids on K_d

Generally, the extraction mechanism of TODGA as a neutral chelating agent to metallic ions is direct and uncomplicated. According to Hecke and Goethals’ report, diglycolamide (DGA) in the TODGA chelating agent contains three oxygen atoms that vigorously capture the metallic ions, so it acts as a tridentate ligand^[23]. While various species such as M⁴⁺, MO²⁺, [M(OH)]³⁺, [M(OH)₂]²⁺, [M(OH)₃]⁺, [M(OH)₄] and [M(OH)₅][−] may be yielded since Zr(IV) and Hf(IV) are both hydrolysable and polymeric in hydrochloric acid solutions (M represents Zr or Hf)^[24,25]. The reactions of zirconium and hafnium in water were the subjects of much controversy. Aqueous solution chemistry and hydrolytic polymerization of their aqueous metallic ions have been reported in several papers^[26–29]. So in order to estimate the optimum conditions for the separation between Zr(IV) and Hf(IV), the uptake experiment was carried out with three kinds of

inorganic acids in the concentration range from 0.1 mol/L to 8 mol/L. A higher pH value was not examined because of the precipitation of Zr(IV) and Hf(IV) at pH >2^[30].

As the results, the distribution coefficients of zirconium and hafnium as a function of acid concentration are shown in Fig.4.

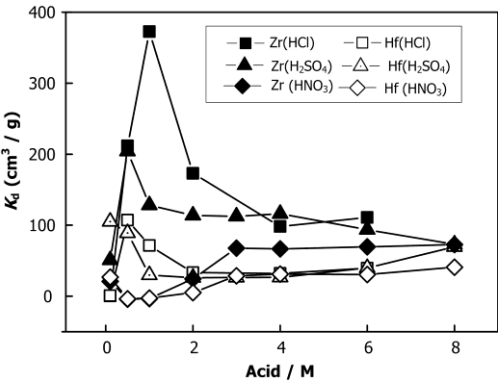


Fig.4 K_d of Zr(IV) and Hf(IV) in different acid solutions with TODGA/SiO₂-P adsorbent. V/m: 100 cm³/g; [Metal]: 2.5 mmol/L; 298 K; Speed: 120 r/min; 24 h.

It was obvious that the TODGA/SiO₂-P adsorbent had a larger separation factor in the chloride system than those in the other two acid systems. The situation is complicated, one reason for this phenomenon may be explained as the stronger complexation of zirconium and hafnium metallic ions with the chloride ions at low acidities. So adsorption behaviors of the adsorbent in batch experiment were evaluated in hydrochloric acid solution.

Combining X-ray absorption spectroscopy (XAFS) and nano-electrospray mass spectrometry (ESI-MS), Walther *et al.* investigated polynuclear species of zirconium in acidic aqueous solution at $0 < \text{pH} < 3$ for $[\text{Zr}] = 1.5\text{--}10 \text{ mmol/L}$. While the monomer remained a minor species, the degree of polymerization increased and the formations of tetramers, pentamers, octamers and larger polymers were observed with increasing pH^[26]. Johnson *et al.* studied hydrolytic behaviors of ca. 0.05 mol/L Zr(IV) and Hf(IV) at the acidity of 0.5–5 mol/L HCl^[27]. As a conclusion, Hf(IV) was probably either a trimer or tetramer and the degree of polymerization was relatively independent of Hf(IV) and HCl concentration in the range of 0.5–2 mol/L HCl. While at acidities of 0.2 mol/L or lower, Hf(IV) was more highly polymerized and polydisperse. In the range of 0–2 mol/L HCl, polymerization of Zr(IV) was similar. The principal difference is that Zr(IV) was more highly aggregated than Hf(IV) at the lower acidity.

As shown in Fig.5, the adsorption of Zr(IV) and Hf(IV) onto TODGA/SiO₂-P adsorbent emerged a similarity and the K_d value tended to change greatly with a parabolic trend when increasing HCl concentration of 0.1–6 mol/L. The maximum K_d value was obtained at about 0.8 mol/L and 0.5 mol/L HCl for Zr(IV) and Hf(IV), respectively. These results indicate that TODGA had a relatively greater extracting ability with the trimer or tetramer of Zr(IV) and Hf(IV) in HCl solution. At the same acidity, Zr(IV) had a higher K_d than that of Hf(IV) probably for the reason that Zr(IV) was more highly aggregated than Hf(IV) at the lower acidities mentioned above. Under the higher pH conditions, polymerization increased and the formation of tetramers, pentamers, octamers and larger polymers decreased the extraction of Zr(IV) and Hf(IV) hydrolyzed species^[26,27]. The drop of K_d

for both elements at higher HCl concentration may be due to a higher degree of protonation for the extractant. On the other hand, it was also possible that the high concentration HCl restricted hydrolyzing and polymerizing of Zr(IV) and Hf(IV) metallic ions to form trimer or tetramer. The findings indicate that the TODGA/SiO₂-P adsorbent has stronger adsorption and higher selectivity for Zr(IV) over Hf(IV), and maximum separation acidity is 0.8–1.5 mol/L HCl.

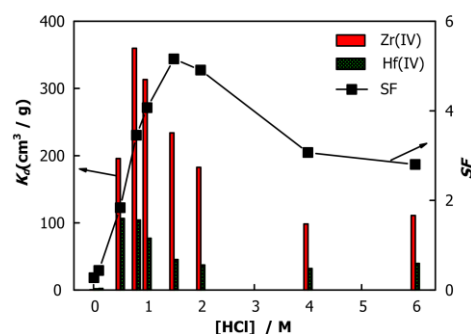


Fig.5 Effect of HCl concentration on SF. V/m: 100 cm³/g; [Metal]: 2.5 mmol/L; 298 K; Speed: 120 r/min; 24 h.

3.4 Adsorption isotherms

Adsorption isotherms were obtained within a wide range of initial total concentrations at two different temperatures, as shown in Fig.6. From the results, we can derive the conclusion that the adsorbent had a larger adsorption capacity to Hf(IV) than Zr(IV) in a single component solution and adsorption capacity to both ions-increased with temperature rising.

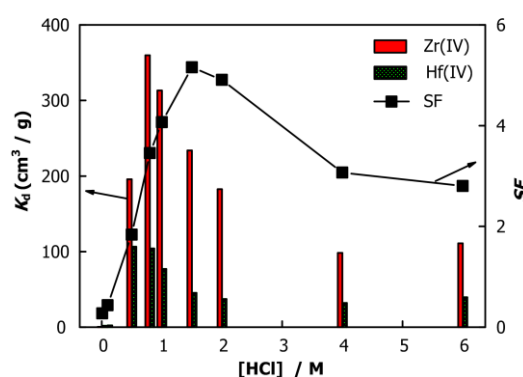


Fig.6 Adsorption isotherms of Zr(IV) and Hf(IV) with TODGA/SiO₂-P adsorbent [HCl]: 1 mol/L; V/m: 100 cm³/g; 24 h; Speed:120 r/min.

When adsorption achieved saturation, theoretical isotherm models of Freundlich equation and Langmuir equation were adopted to explore adsorption mechanism and calculate maximum

capacity of the adsorbent. The Langmuir equation assumes that the adsorption process is a monolayer adsorption on a homogeneous surface. Meanwhile, the Freundlich equation is an empirical equation applied to monolayer adsorption on the heterogeneous surface [31,32]. They are expressed as below, respectively.

$$C_e/Q_e=C_e/Q_{max}+(1/K_LQ_{max}) \tag{7}$$

$$\ln Q_e=\ln C_e/n+\ln K_f \tag{8}$$

where C_e (mmol dm⁻³) is the equilibrium concentrations of Zr and Hf in aqueous phase; Q_e (mmol g⁻¹) and Q_{max} (mmol g⁻¹) denote the adsorption amounts at equilibrium state and the maximum adsorption state; K_L (dm³ mmol⁻¹) is the Langmuir constant which relates to the energy of adsorption; $1/n$ is the Freundlich isotherm exponent constant which relates to the adsorption intensity; K_f (mmol g⁻¹) is the Freundlich constant.

Figs.7A and 7B show the linearized Langmuir and Freundlich adsorption isotherms, respectively. The parameters of two isotherms obtained from experimental data and the related correlation coefficients (R^2) are presented in Table 2. Better correlation coefficient (0.99) obtained from the Langmuir isotherm suggested that the adsorption of Zr and Hf were monolayer adsorption controlled by homogeneous active sites of the adsorbent. Since K_L reflects the affinity between the active sites and

metallic ion, the gradually increase of K_L value in Langmuir isotherm with the temperature indicates a positive activation energy. Meanwhile, we can surely draw the conclusion that Zr(IV) had a more stronger affinity than Hf(IV) to the TODGA/SiO₂-P adsorbent.

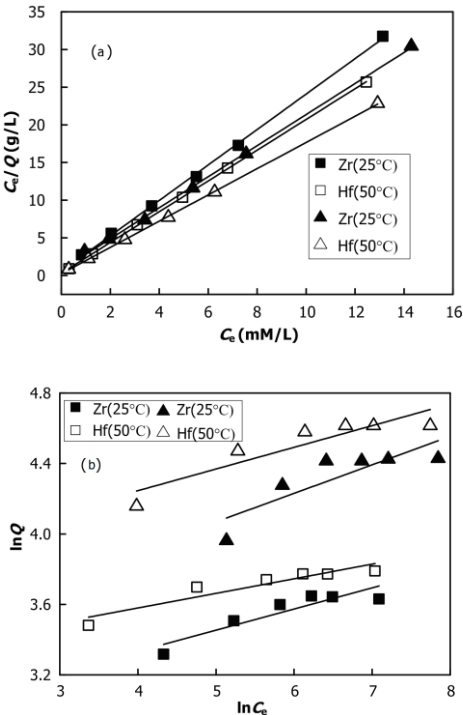


Fig.7. Isotherm fitting for Zr and Hf adsorptions by Langmuir model (a) and Freundlich model and(b) V/m: 100 cm³/g; [HCl]: 1mol/L; Speed:120r/min; 24 h.

Table 2 Fitting parameters of isotherm for Zr and Hf adsorptions onto the TODGA/SiO₂-P adsorbent

Metal	T (K)	Langmuir isotherm				Freundlich isotherm		
		Q_e (mmol/g)	Q_{max} (mmol/g)	k_L (L/mmol)	R^2	K_f (mmol/g)	n	R^2
Zr	298	0.47	0.485	4.18	0.99	17	8.3	0.83
	323	0.566	0.574	6.67	0.99	26	12.1	0.88
Hf	298	0.414	0.425	2.73	0.99	26	6.2	0.72
	323	0.485	0.49	6.05	0.99	43	8.1	0.84

3.5 Adsorption thermodynamics

The values of standard ΔH° and ΔS° for Zr and Hf in adsorption reactions were calculated from the slopes and intercepts of the linear van't Hoff equation as shown below (Fig.8).

$$\ln K_d=(-\Delta H^\circ/RT)+(\Delta S^\circ/R) \tag{5}$$

The Gibbs free energy of the adsorption, ΔG° was calculated from

$$\Delta G^\circ=\Delta H^\circ-T\Delta S^\circ \tag{6}$$

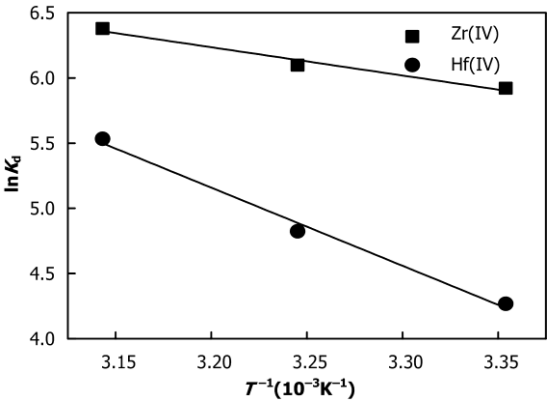


Fig.8 Linear least square plots for obtaining thermodynamic parameters. V/m: 100 cm³/g; [Metal]: 2.5 mmol/L; [HCl]: 1mol/L; Speed: 120 r/min; 24 h.

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All the thermodynamic parameters are summarized in Table 3. As shown in the table, negative ΔG° values indicate that the adsorption processes took place spontaneously. The enthalpy change values for both metallic ions are positive, indicating that the adsorptions of zirconium and hafnium are endothermic processes. It is a notable phenomenon because adsorption processes for some trivalent rare earths using this adsorbent are exothermal^[29]. The system is complex. One reasonable

interpretation may be due to the facilitation of the metal ions hydrolysis when raising temperature. Also, the data $|\Delta H^\circ| < |-T\Delta S^\circ|$ in Table 3 showed that the adsorption processes were dominated by entropic changes rather than enthalpy changes. By comparing the enthalpy change values, it is obvious that temperature has a greater influence on the adsorption of Hf(IV) than that of Zr(IV), which could be controlled to increase the adsorption difference for better separation.

Table 3 Thermodynamic parameters of Zr and Hf adsorptions onto the TODGA/SiO₂-P adsorbent

T(K)	Zr				Hf			
	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G/\text{kJ}\cdot\text{mol}^{-1}$	$T\Delta S/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G/\text{kJ}\cdot\text{mol}^{-1}$	$T\Delta S/\text{kJ}\cdot\text{mol}^{-1}$
298	18	109.5	-14.6	32.6	49.8	202.9	-10.5	60.3
308	18	109.5	-15.7	33.7	49.8	202.9	-12.5	62.3
318	18	109.5	-16.8	34.8	49.8	202.9	-14.6	64.4

4 Conclusion

Several kinds of macroporous silica-based adsorbents were synthesized and the TODGA/SiO₂-P adsorbent was found to have a higher adsorption selectivity to Zr(IV) than that of Hf(IV). The adsorbent was characterized by means of SEM and TG-DTA. The uptake behaviors in three kinds of inorganic acid solutions were investigated and the adsorption mechanism was attempted to be explained. By fitting different isotherm models and calculating thermodynamic parameters, the adsorption procedures for both metals were found to be endothermic with a monolayer adsorption on a homogeneous surface. The TODGA adsorbent could be promising for the separation between Zr(IV) and Hf(IV) due to its good adsorptive selectivity in preliminary experiment.

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